

Carbon Nanofibers: A Unique Catalyst Support Medium

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Received: September 13, 1994; In Final Form: October 31, 1994[†]

When used as a catalyst support medium, graphitic carbon nanofibers have been found to exert a dramatic effect on the performance of Fe–Cu (7:3) and Fe particles when such systems were heated in hydrocarbon environments. The catalytic activity of these systems, for the conversion of hydrocarbons, was considerably higher than that found when the Fe-containing particles were supported on either active carbon or γ -alumina and treated under the same conditions. TEM analysis indicated that this enhancement in activity could not be accounted for by a particle size effect. Other possible explanations for this unusual behavior are discussed.

Introduction

The recent discovery of novel carbon structures including fullerenes and nanotubes that are produced by arc discharge of graphite electrodes in the presence of inert gases has generated tremendous excitement in the scientific community.^{1–10} It has been speculated that because of the unique structure of carbon nanotubes, the material may possess extraordinary physical and chemical properties. Current research efforts in this area are being focused on the utilization of catalysts to control the size and morphology of the nanotubes and also improve the efficiency of the process.

Catalytically grown carbon nanofibers are one of the newly developed materials that are produced by the decomposition of selected hydrocarbons over metal particles.¹¹ The material possesses a unique combination of physical and chemical properties imparted by the presence of graphitic platelets, the arrangement of which can be tailored to produce a variety of conformations.¹² In the growth process, the hydrocarbon is dissociatively chemisorbed at the surface of the metal particle; carbon atoms proceed to diffuse through the particle and precipitate at particular crystal faces to generate the nanofiber. Thus, the orientation adopted by the crystal is the crucial parameter that determines not only the alignment of the graphite platelets but also the degree of perfection of the crystallites.^{13,14} The particle size of the metal catalyst is a further variable that affects the conformation of these structures; particles with diameters smaller than 25 nm will tend to produce nanotubes, whereas larger particles usually generate solid nanofibers. The typical lengths of carbon nanofibers are in the range 5–100 μm , and diameters are 5–1000 nm. Previous studies from this laboratory have shown that carbon nanofibers are produced with surface areas of up to 300 m^2/g , which can be enhanced by careful activation in CO_2 to about 700 m^2/g .¹⁵ In addition, these structures have low electrical resistivities, which are very close to that of graphite (1375 $\mu\Omega\cdot\text{cm}$).¹⁶ In summary, carbon nanofibers can be considered as a high surface area graphitic material.

In the current investigation we have attempted to exploit the potential of carbon nanofibers as a catalyst support. We have conducted a preliminary series of experiments in which the catalytic hydrogenation activity of Fe–Cu (7:3) particles supported on carbon nanofibers was compared to that found for the same loading of the bimetallic on activated carbon and γ -alumina. In a second set of experiments attention was focused

on the catalytic behavior of iron particles supported on these materials. In both cases the conversion of ethylene to gaseous and solid products, respectively, was used as a probe reaction.

Experimental Section

The carbon nanofibers used in this investigation were produced from the interaction of iron powder with a $\text{CO}-\text{H}_2$ mixture at 600 °C. It has been established that the nanostructures formed from this process are highly graphitic in nature and had a BET surface area of 184.0 m^2/g .¹⁷ Following the growth of carbon nanofibers, the metal particles present within the structures were removed by dissolution in 1.0 M HCl prior to impregnation of the desired iron–copper or iron catalyst precursor salts. Activated carbon was obtained from Norit and γ -alumina from Degussa and had BET surface areas of 516.6 and 91.2 m^2/g , respectively. Introduction of an iron rich bimetallic phase onto these three supports was accomplished by addition of the respective metal nitrates, mixed in the desired ratio in ethanol using the incipient wetness technique followed by suitable calcination and reduction steps to generate a high dispersion of discrete Fe–Cu (7:3) particles at a 5 wt% loading. Similar procedures were employed for the preparation of supported Fe catalysts; however, in these cases the loading was increased to 10 wt%. All reduced catalyst samples were carefully passivated by cooling to room temperature in He and then treated in a 2% CO_2 –He mixture for 1 h before removal from the reactor to prevent bulk oxidation of the metal particles.

Experiments designed to compare the hydrogenation activity of the three supported Fe–Cu catalyst systems were carried out in a Pyrex tube reactor (2.5 cm i.d. and 40 cm long) consisting of two sections separated by a porous glass disc, located in a vertical tube furnace and connected to an on-line gas chromatography unit. Catalyst samples (100 mg) were dispersed on the porous disc and placed in the center of the heated zone of the reactor. Initially, the catalysts were reduced in 10% H_2 /He at 400 °C for 4.0 h and then brought to the desired reaction temperature. Following this step, a $\text{C}_2\text{H}_4/\text{H}_2$ (1:4) mixture was passed over the catalyst at a flow rate of 200 mL/min at temperatures over the range 80–180 °C for periods of up to 3.0 h. The relative activity of each catalyst sample was determined from the percent conversion of the olefin to ethane. In a further series of experiments the catalyst samples were treated in a $\text{CO}/\text{C}_2\text{H}_4/\text{H}_2$ (2:2:1) mixture at 600 °C at a flow rate of 200 mL/min for a period of 2.5 h. These reactions were performed in a horizontal quartz tube reactor system, and in addition to measuring the gas phase products at regular intervals,

[†] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

The patents and/or publications submitted herewith are set forth on the attached Form PTO-1449.

Applicants certify that references US 6350364B1 and US 2002/0027081B1 submitted with this disclosure were first cited in a communication from a foreign patent office dated November 12, 2004, which communication is enclosed, not more than three months prior to the filing of this Supplemental Information Disclosure Statement.

If the fee of \$180.00 is due, the Commissioner is hereby authorized to charge the sum of \$180.00 due under 37 CFR § 1.17(p) pursuant to § 1.97, and any other fee necessary to make this submission timely, to the Deposit Account No. 20-0782/AMAT/8241/KMT.

Respectfully submitted,



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Application Number	10/616,097
Filing Date	JULY 8, 2003
First Named Inventor	SUN, et al.
Art Unit	1753
Examiner Name	UNKNOWN

Attorney Docket Number

AMAT/8241/PPC/ECP/RKK

U.S. PATENT DOCUMENTS

Examiner Initials *	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number - Kind Code ² (if known)			
	A1	US- 6350364 B1	02/26/2002	Jang	
	A2	US- 2002/0027081 A1	03/07/2002	Nagai, et al.	
	A3	US- 2004/0072419 A1	04/15/2004	Baskaran, et al.	
	A4	US-			
	A5	US-			
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FOREIGN PATENT DOCUMENTS

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Examiner Name	UNKNOWN

Attorney Docket Number

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	C1	International Search Report dated December 11,2004 for corresponding PCT/US2004/021771.	
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